Water-cluster distribution with respect to pressure and temperature in the gas phase

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In spite of decades of extensive studies of water, the experimental information of water clusters larger than the trimer is hardly available yet. To aid the better analysis of certain cluster properties in an experiment, we studied the small-water-cluster distribution (particularly for the minimum-energy structures) in the gas phase. Utilizing the thermodynamic information in the range from the water monomer to the octamer (except for the heptamer) by *ab initio* calculations, we investigated the mole fractions of the water clusters along the vapor pressure of the condensed phase. These mole fractions increase with increasing temperature or pressure, while the higher clusters increase still more. The entropy increment of the cyclic pentamer relative to the cyclic tetramer is particularly small; thus, the cyclic pentamer shows thermodynamically unusual characteristics. For the trimer, the cyclic structure is more stable than the linear structure at temperatures lower than ~400 K, while above this temperature, the latter is more stable due to the entropy effect. Similar phenomena are also expected for the higher clusters. The mole fractions of the higher cyclic clusters are found to be very small in a vapor unless they are uncondensed with insufficient water molecules.

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I. INTRODUCTION

Water is a very fundamental and important substance. To investigate the structure, spectra, and energetics of water and to gain insight into the interaction of water with ions, chemical reagents, and biomolecules, there have been a number of experimental studies of water clusters in isolated systems [1–14] as well as in various chemical environments [15,16]. Yet, in spite of decades of extensive studies, little experimental information of the water clusters is available [1–9], except for the dimer [10–14]. Even for the water dimer there remain unresolved problems such as the structure and binding energy [17–23]. One of the difficulties in water-cluster experiments is due to the fact that the water-cluster distribution is not clearly known with respect to temperature or pressure. Thus, certain properties of the water clusters (such as the binding energies and thermal energies) in equilibrium may not be analyzed accurately. For this reason, we studied thermodynamic energies of small water clusters with *ab initio* calculations including electron correlation.

Although a multitude of theoretical studies of the water monomer and the dimer [17–27] are available, only a few reliable *ab initio* studies for the water clusters higher than the dimer have been reported [28–32]. According to various analytical water-water potential functions [32–42], the water trimer, tetramer, and pentamer are cyclic, whereas the clusters higher than the hexamer are not cyclic. Although all these potentials fail to find that the cyclic hexamer is the global minimum structure, *ab initio* calculations with the double zeta polarization (DZP) basis sets find two nearly isoenergetic hexamer structures, which are cyclic and noncyclic [28]. The cyclic structure is only slightly lower in energy than the noncyclic one.

The octamer has also two isoenergetic structures with the D_{2d} and S_4 symmetries, while the former is slightly lower in energy than the latter at 0 K [35]. Based on these minimum-energy structures (i.e., cyclic structures for $3 \leq n \leq 6$ and D_{2d} structure for $n = 8$), we studied the thermodynamic energies of small water clusters. In the present paper the cyclic trimer through hexamer and the D_{2d} octamer will be simply denoted by the trimer through hexamer and the octamer, unless otherwise specified. In addition to these minimum-energy structures, we studied two other stable energy structures for the trimer and the isoenergetic structures of $n = 6$ and 8.

II. THEORETICAL APPROACH

To find the structures and energetics of the water clusters, we have performed Hartree-Fock (HF) self-consistent-field and second-order Moller-Plesset perturbation (MP2) calculations using the DZP basis sets. The DZP basis sets comprised the Huzinaga-Dunning basis sets [43] with a set of five d orbitals with the exponent 0.85 for O and a set of three p functions with the exponent 1.0 for H. The scaling factor of 1.2 was used for the s functions of H. The calculations were done with the computer program GAUSSIAN90 [44]. The water-cluster geometries were fully optimized for both HF and MP2 calculations, except for the MP2 calculations of the pentamer and octamer. For our data analysis, the MP2 energies calculated at the HF-optimized geometries are also reported, which will be denoted by MP2-HF. The basis-set superposition error correction (BSSEC) was done for all calculations. The thermal energy correction for the MP2-HF was approximated with the HF harmonic vibrational frequencies. Since the cyclic trimer and pentamer have the chiral structures, the entropic energy correc-

tions were approximated with the values of $-RT\ln2$ at temperature T [45], where R is the gas constant.

The effect of the potential flatness along with potential anharmonicity on the thermodynamic energies of the water dimer was found to be significant, but not seriously large at 373 K [17]. The results of cyclic clusters below ~ 300 K can be reliable, which will be discussed later. But, at temperatures higher than ~ 400 K not only anharmonic correction can be significant but also other local minimum structures can have significant statistical distributions, so that thermal corrections based on a harmonic potential approximation near the global minima may not be reliable. This kind of problem can be noted from the flat potential-energy hypersurfaces of the dimer [25,27]. Nevertheless, up to the range of the critical temperature of water (647 K) [46] such an approximation may provide an idea of the distribution of a certain cluster which keeps almost the original minimum-energy structure.

III. THERMODYNAMIC QUANTITIES OF THE WATER CLUSTERS

Table I shows the thermodynamic energy change when 1 mol of the water monomers change to the clusters $(H_2O)_n$ (for $1 \le n \le 6$ and $n = 8$). The table lists ΔE_e and ΔE_o, which are the binding energies without and with zero-point energy correction at 0 K, respectively. The table also lists ΔE_r, ΔH_r, ΔA_r, ΔG_r, and ΔS_r, which are the changes of the internal energies, enthalpies, Helmholtz free energies, Gibbs free energies, and entropies at 298 K and 1 atm, respectively. Here the subscript r denotes the state at room temperature (298 K) and 1 atm. The entropic corrections for chiral molecules ($n = 3$ and 5) were approximated with $R\ln2n^{-1} = 1.38n^{-1}$ cal mol^{-1}K^{-1} for ΔS and $-RT\ln2n^{-1} = -0.41n^{-1}$ kcal/mol for both ΔA_r and ΔG_r [45].

The experimental ΔE_e and ΔG(373 K) of the dimer are -5.4 ± 0.7 and 3.34 kcal/(mol-dimer), respectively [13]. Without BSSEC the ΔE_e and ΔG(373 K) predicted by the MP2-HF (DZP) are -6.22 and 2.86 kcal/(mol-dimer), while with BSSEC the two values are -5.14 and 3.94 kcal/(mol-dimer), respectively. Considering the internal hindered rotation and the potential flatness of the dimer [25,27], the free energies will be predicted to be much lower [by 0.72 kcal/(mol-dimer) or 0.36 kcal/(mol-monomer) at 373 K [17]]. Consequently, the calculations with BSSEC give much more realistic values for both ΔE_e and ΔG of the dimer. More detailed MP2 calculations using various large basis sets also showed that the

TABLE I. Thermodynamic energies for $H_2O \Longrightarrow (1/n)(H_2O)_n$. See the text for the notations. The energies with the BSSEC are in parentheses. The energies and entropy are in kcal/mol and cal mol^{-1}K^{-1}, respectively.

Energy calc.	sym	n = 2 C_s	3[a] C_1	4 S_4	5[a] C_1	6 S_6	8 D_{2d}
ΔE_e	HF	$-2.52(-2.37)$	$-4.94(-4.50)$	$-6.49(-5.97)$	$-6.88(-6.40)$	$-7.15(-6.67)$	$-8.28(-7.46)$
	MP2-HF	$-3.11(-2.57)$	$-6.33(-5.19)$	$-8.30(-6.94)$	$-8.70(-7.37)$	$-8.99(-7.64)$	$-10.85(-8.81)$
	MP2	$-3.18(-2.52)$	$-6.58(-5.10)$	$-8.63(-6.89)$		$-9.33(-7.59)$	
ΔE_0	HF	$-1.44(-1.29)$	$-3.13(-2.69)$	$-4.35(-3.83)$	$-4.77(-4.29)$	$-4.99(-4.50)$	$-5.66(-4.84)$
	MP2-HF	$-2.03(-1.49)$	$-4.52(-3.38)$	$-6.16(-4.79)$	$-6.59(-5.26)$	$-6.83(-5.48)$	$-8.23(-6.20)$
	MP2	$-2.02(-1.35)$	$-4.60(-3.11)$	$-6.36(-4.61)$		$-7.03(-5.29)$	
ΔE_r	HF	$-1.36(-1.21)$	$-3.25(-2.81)$	$-4.52(-4.00)$	$-4.84(-4.36)$	$-5.03(-4.54)$	$-5.89(-5.07)$
	MP2-HF	$-1.95(-1.41)$	$-4.63(-3.50)$	$-6.33(-4.96)$	$-6.66(-5.32)$	$-6.87(-5.52)$	$-8.46(-6.42)$
	MP2	$-1.99(-1.33)$	$-4.85(-3.36)$	$-6.66(-4.91)$		$-7.21(-5.47)$	
ΔH_r	HF	$-1.66(-1.51)$	$-3.65(-3.21)$	$-4.96(-4.44)$	$-5.31(-4.83)$	$-5.52(-5.03)$	$-6.41(-5.59)$
	MP2-HF	$-2.25(-1.71)$	$-5.03(-3.90)$	$-6.77(-5.40)$	$-7.13(-5.79)$	$-7.36(-6.01)$	$-8.98(-6.94)$
	MP2	$-2.29(-1.63)$	$-5.25(-3.76)$	$-7.10(-5.35)$		$-7.70(-5.96)$	
ΔA_r	HF	$1.59(1.74)$	$1.82(2.26)$	$1.89(2.41)$	$1.56(2.04)$	$1.93(2.41)$	$2.35(3.17)$
	MP2-HF	$1.00(1.54)$	$0.44(1.57)$	$0.08(1.44)$	$-0.26(1.07)$	$0.09(1.44)$	$-0.22(1.81)$
	MP2	$1.15(1.82)$	$0.62(2.10)$	$0.12(1.86)$		$-0.15(1.89)$	
ΔG_r	HF	$1.29(1.44)$	$1.43(1.87)$	$1.45(1.97)$	$1.09(1.57)$	$1.44(1.92)$	$1.83(2.65)$
	MP2-HF	$0.70(1.24)$	$0.05(1.18)$	$-0.36(1.00)$	$-0.73(0.60)$	$-0.40(0.95)$	$-0.74(1.30)$
	MP2	$0.85(1.52)$	$0.23(1.71)$	$-0.32(1.42)$		$-0.64(1.40)$	
ΔS_r	HF	-9.90	-17.02	-21.48	-21.45	-23.32	-27.64
	MP2-HF	-9.90	-17.02	-21.48	-21.45	-23.32	-27.64
	MP2	-10.50	-18.34	-22.72		-24.70	

[a]Owing to the chirality of the molecules, the entropies and free energies were corrected by $1.38n^{-1}$ cal mol^{-1}K^{-1} and $-0.41n^{-1}$ kcal/mol, respectively.

free energies without BSSEC were too low and were much too dependent upon the basis sets used, whereas those with BSSEC were somewhat high, but rather independent of the basis sets [17]. Thus, although basis-set superposition errors are somewhat overestimated, energies with BSSEC can still be more reliable. This is further supported by many recent calculational results in favor of BSSEC [19,20].

In Table I, the MP2 energies for $n = 5$ and 8 are not available, but the MP2-HF energies are very close to the MP2 energies; thus, our discussion will be based on the MP2-HF energies with BSSEC, unless otherwise specified. From the MP2-HF values with BSSEC in the table, it is interesting to note that the ΔG_r (0.60 kcal/mol) of the pentamer is by far the smallest among the clusters of $n = 2$–6 and 8. Although the ΔG_r of the pentamer is 0.35 kcal/mol lower than the hexamer, the ΔE_e of the pentamer (-7.37 kcal/mol) is 0.27 kcal/mol higher than that of the hexamer. Thus, the pentamer is less stable than the hexamer at very low temperatures, whereas the former is more stable near room temperatures. Figure 1 shows the temperature dependency of the MP2-HF-predicted ΔG for the polymerization of $H_2O \Longrightarrow (1/n)(H_2O)_n$. In the range of 180–270 K the pentamer has the lowest ΔG among $n = 1$–6 and 8. In the range of 270–355 K the ΔG of the pentamer is the second lowest only to that of the monomer. This unusual characteristics of the pentamer is due to the small entropy decrement (ΔS) for the change from the tetramer to the pentamer.

In Fig. 2, which shows the $\Delta S (n-1 \rightarrow n)$ for $(H_2O)_{n-1} + H_2O \Longrightarrow (H_2O)_n$, the entropy decrements for the changes of $1 \rightarrow 2$ and $4 \rightarrow 5$ are much smaller than those for the changes of $2 \rightarrow 3$, $3 \rightarrow 4$, and $5 \rightarrow 6$. The small entropy decrement for $4 \rightarrow 5$ indicates that the pentamer has less geometrical strain than other clusters. Namely the monomer bond angle $\angle H$—O—H ($\sim 105°$, which reflects the sp^3 tetrahedral shape) is very close to the angle between three adjacent oxygen atoms of the pentamer ($\sim 107°$). Thus, the hydrogen bondings between adjacent water molecules in the pentamer are possible without much strain, so that the pentamer has particularly large entropy per water molecule compared with the tetramer and hexamer.
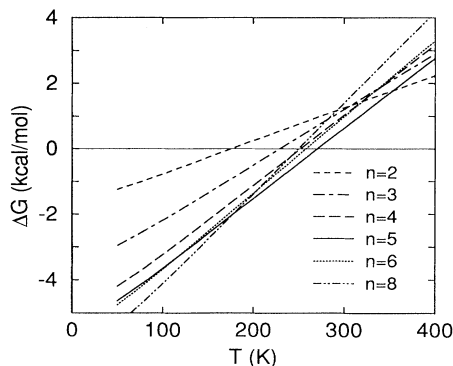

FIG. 2. Entropy increment (ΔS for $n - 1 \rightarrow n$) vs T for $(H_2O)_{n-1} + H_2O \Longrightarrow (H_2O)_n$.

Let us consider the temperature (T) or pressure (P) dependency of ΔG for $H_2O \Longrightarrow (1/n)(H_2O)_n$ in the gas phase which is in equilibrium with the condensed phase. As shown in Fig. 3, for each cluster the slope of the curve for ΔG vs T (or $\log_{10} P$) changes abruptly at $T = 273$ K (or $P = 4.6$ Torr) due to the latent heat that ice changes to liquid water (1.4 kcal/mol [47]). With the conventional thermodynamic notations such as V (volume), V_g (gas volume), R (gas constant), and H_λ (latent heat for boiling or sublimating), we studied the abrupt slope change as follows. The ideal gas approximation for 1 mol of water clusters in the phase equilibrium gives that

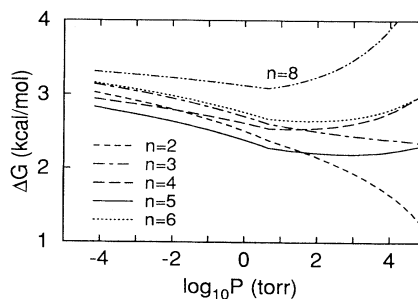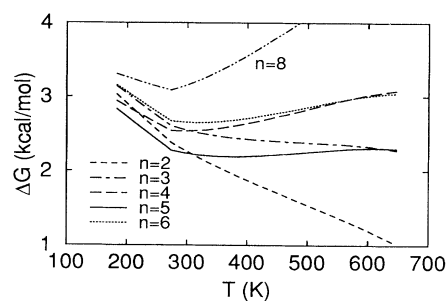$$\frac{dP}{dT} = \frac{H_\lambda}{T \Delta V} \simeq \frac{H_\lambda}{TV_g} \simeq \frac{H_\lambda P}{RT^2}$$

FIG. 3. Gibbs free-energy change (ΔG) for $H_2O \Longrightarrow (1/n)(H_2O)_n$ in the vapor-water or vapor-ice phase equilibrium: ΔG vs boiling or subliminating temperature (T) and ΔG vs vapor pressure (P).
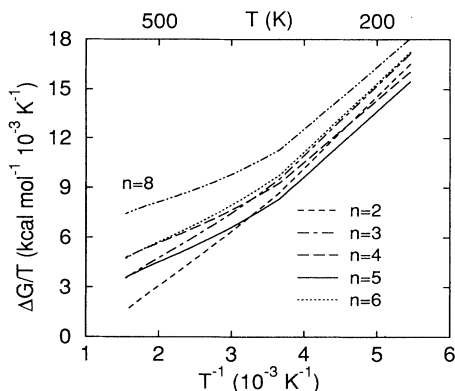

FIG. 1. Helmholtz free-energy change (ΔA) vs temperature (T) for $H_2O \Longrightarrow (1/n)(H_2O)_n$.

FIG. 4. $\Delta G/T$ vs T^{-1} for $H_2O \Longrightarrow (1/n)(H_2O)_n$ in the vapor-water or vapor-ice equilibrium.

or

$$Rd \ln P \simeq -H_\lambda d\left[\frac{1}{T}\right].$$

Since

$$d\left[\frac{G}{T}\right] = \frac{dG}{T} - \frac{G}{T^2}dT = Hd\left[\frac{1}{T}\right] + \frac{V}{T}dP,$$

we have

$$d\left[\frac{G}{T}\right] \simeq Hd\left[\frac{1}{T}\right] + Rd \ln P = (H - H_\lambda)d\left[\frac{1}{T}\right].$$

Then, for the ΔG for $H_2O \Longrightarrow (1/n)(H_2O)_n$, we have the following relation:

$$\frac{d(\Delta G/T)}{d(1/T)} \simeq \Delta H - \frac{n-1}{n}H_\lambda,$$

where $d(\Delta G) = G((1/n)(H_2O)_n) - G(H_2O)$ and $d(\Delta H) = H((1/n)(H_2O)_n) - H(H_2O)$. Thus, in Fig. 4 the curve slopes for $(\Delta G/T)$ vs $(1/T)$ represent $\{\Delta H - [(n-1)/n]H_\lambda\}$. Then, one can note that the abrupt changes of the curve slopes at 273 K are due to $[(n-1)/n]H_\lambda$.

IV. THE WATER-CLUSTER DISTRIBUTION

The information of the mole fractions of the water clusters is very important to analyze the cluster experimental data. To maximize the mole fractions at a specified temperature, the clusters should not be condensed; otherwise, in the condensed phase small clusters would coagulate together into much larger clusters which are energetically more stable. Thus, the clusters need to be at the highest pressure of the gas phase, i.e., at the pressure in the vapor-liquid or vapor-ice phase equilibrium. Thus, we study the temperature or pressure dependency of mole fractions of the clusters in the vapor at the phase equilibrium.

Using the calculated ΔG in the vapor-water or vapor-ice equilibrium, we obtained the mole fractions (X_n) of the n-membered water clusters with respect to the boiling

or sublimating temperature (T) or the vapor pressure (P): $X_n = X_1^n \exp[-\Delta G/RT]$. Figure 5 shows the mole fractions of the cyclic water clusters ($3 \leq n \leq 6$) and the D_{2d} octamer ($n=8$) as well as the dimer along the vapor pressure (and the corresponding temperature) of the condensed phase. The mole fractions of the isoenergetic hexamer (with C_1 symmetry) and octamer (with S_4 symmetry) were also studied. The C_1 hexamer has almost the same mole fraction as the cyclic hexamer over all temperature ranges. The S_4 octamer is 0.05 kcal/mol higher in energy than the D_{2d} octamer at 0 K. But, over 40 K, the former has lower free energy than the latter. At 400 K, the former is 2.3 times more populated than the latter. However, the figures for these isoenergetic structures are not shown in Fig. 5 only for visual purpose, because their curves shown in logarithmic scale of mole fraction are not significantly different from those of the minimum-energy structures. From Fig. 5, we find that the larger the cluster size is, the smaller its mole fraction is over the whole temperature (or pressure) range, except for the tetramer-pentamer case. With increasing temperature the mole fraction of the pentamer increases much more than that of the tetramer. Although at low temperatures the pentamer is less populated than the tetramer, at very high temperatures the pentamer is more populated. As noted earlier, however, the calculation results at temperatures higher than ~ 400 K may not be reliable, which will be discussed later.

In Fig. 5, it is interesting to note that for each cluster the logarithm of the mole fraction changes almost linearly with the logarithm of the vapor pressure. This result is partially consistent with the assumption made in experiments that the water-cluster mole fractions vary approxi-
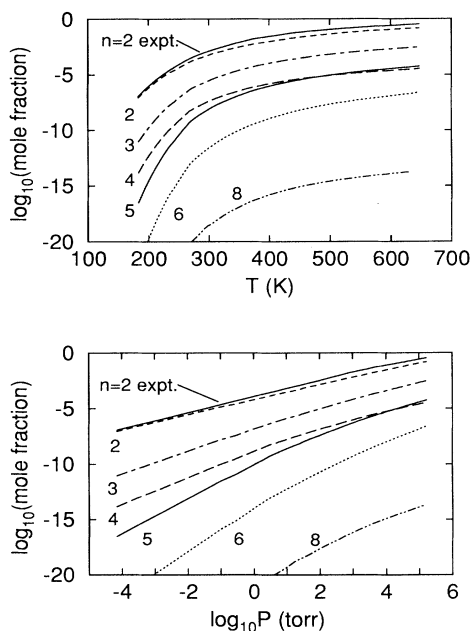

FIG. 5. Mole fractions of the water clusters in vapor with respect to the boiling or subliminating temperature (T) or the vapor pressure (P).

mately linearly with partial vapor pressure [48,49]. But, the slope of $\log_{10}(X_n)$ vs $\log_{10}(P)$ is not 1 for all the clusters. The slopes for the trimer and tetramer are almost 1. But, the slope for the dimer is somewhat less than 1, while those for the pentamer and hexamer are somewhat larger than 1. However, it should be noted that the experiment includes the conformers other than the cyclic structures, while our calculation results are based only on the cyclic clusters (for $n = 3-6$), the D_{2d} octamer, and the isoenergetic hexamer and octamer.

One existing experimental datum for the mole fraction of the dimer [50] is close to our results, as shown in Fig. 5. In particular, our previous *ab initio* calculations using very large basis sets (13,8,4,2/8,4,2) along with the MP2 harmonic vibrational frequencies by the basis sets [7,4,2,1/4,2,1] predicted that the $\Delta G(373\ K)$ is 4.44 kcal/(mol-dimer) [17]. When the internal hindered rotation and anharmonicity of the potential hypersurfaces were taken into account, the $\Delta G(373\ K)$ is lowered by 0.72 kcal/(mol-dimer), thus reduced to 3.72 kcal/(mol-dimer). Then, this correction makes the mole fraction of the dimer at 373 K increase from 0.0025 to 0.0066. This value can be compared with the experimental value of 0.011 [with $\Delta G = 3.34$ kcal/(mol-dimer)] and the MP2-HF (DZP)-predicted value of 0.0049 [$\Delta G = 3.94$ kcal/(mol-dimer)]. Since the mole fraction of the dimer depends on the ΔG sensitively, an accurate prediction of the mole fraction may not be possible, as long as the basis-set superposition error tends to be overestimated. Only very large basis sets which make the BSSEC negligible can predict the accurate ΔG and thus the correct mole fraction. The aforementioned large-basis-set calculation predicted that the $\Delta G(298\ K)$ at the pressure of the vapor-water equilibrium (24 Torr) is 4.97 kcal/(mol-dimer) with the harmonic potential approximation, and is 4.54 kcal/(mol-dimer) with the corrections [of 0.43 kcal/(mol-dimer)] for both the hindered rotation and the potential anharmonicity. Even though the flat potential of the dimer gives a significant change in free energy, this free-energy change does not alter our discussion seriously. In particular, the free-energy lowering of the dimer was mainly due to the internal hindered rotation [0.53 kcal/(mol-dimer) at 373 K and 0.29 kcal/(mol-dimer) at 298 K], while the anharmonic correction was only 0.19 kcal/(mol-dimer) or 0.095 kcal/(mol-monomer) at 373 K and 0.13 kcal/(mol-dimer) or 0.065 kcal/(mol-monomer) at 298 K. Although the cyclic clusters and D_{2d} octamer may have the potential-energy hypersurfaces with multiminima, the internal free rotations are almost forbidden due to the closed structures. Thus, their free-energy lowering only due to the anharmonic potentials would not be large. In addition, the effects of multiminima on the free energy may not be large for small n. For example, let us consider a symmetric double-well potential due to two degenerate conformations. Then, the free-energy lowering is not more than $RT \ln 2$ (0.41 kcal/mol at 298 K) [45]. If there is such a double well in a cluster with n water molecules, the free-energy lowering per water monomer is not more than $0.41n^{-1}$ kcal/mol at 298 K (e.g., 0.07 and 0.05 kcal/mol for the isoenergetic hexamers and octamers, respectively). This energy lowering is

significant, but not seriously large. We will also show later that for $n = 3$ the effect of the three different minimum-energy structures on free energy is small for $T < 400$ K. Similarly, the effect of the flatness of potential-energy hypersurface on the free-energy lowering for small clusters would not be large unless at very high temperatures other possible conformations such as open structures with high degree of free rotation are highly populated. However, we conjecture that for very large n, the effects of numerous multiminima along with flat potential on the free-energy lowering would be great, which may be related to the condensed phase.

Overall, we expect that for small clusters the flat potential problem is much less serious below 300 K. Thus, our results can be particularly useful below 300 K, while they can be semiquantitatively correct between 300 and 400 K. Above 400 K, our data may not be reliable, but we plotted the mole fractions up to the critical state (647 K, 1.655×10^5 Torr) so that we can have a rough idea of the distributions of the clusters which are similar to the original minimum structures.

The water-cluster distribution by the molecular-beam experiment along with the mass spectrometer was reported by Vernon *et al.* at certain temperatures [4]. But, the molecular-beam experiment was based on the nonequilibrium state which did not have enough water to be condensed. Without sufficient water, the clusters do not condense even above the vapor pressure, but remain with finite size. Therefore, their results cannot be directly compared with our results, which are based on the equilibrium system with enough water molecules so as to be condensed above the vapor pressure. Further, Vernon *et al.* noted in their paper that their results may not be reliable due to a lot of uncertainty such as evaporation of one or two water molecules from the clusters during the electron bombardment ionization process.

Very recently, Mo, Yanez, and Elguero [31] reported the *ab initio* study of the water trimers. They predicted the binding energies with the MP2[6-311+$G(d,p)$] calculation without BSSEC and the vibrational frequencies with the HF[6-311++$G(2d,2p)$] calculation [31]. Utilizing this information, we show in Fig. 6 the mole fractions of the three stable conformers of the trimer: linear, unidirectional cyclic, and nonunidirectional cyclic structures, which are denoted in Ref. [31] by 1a, 11, and 10, respectively. We made the entropic corrections for the chiralities of the two cyclic structures. The mole fraction of the linear structure becomes larger when $T > 480$ K. When the internal free rotations of the two terminal water molecules are taken into account, the linear structure will be more populated than the cyclic conformer when $T > 400$ K. At 500 K the successive entropy for the cyclic trimer is -32 cal mol^{-1}K^{-1}, while that for the linear trimer is -16 cal mol^{-1}K^{-1}. The latter value is in good agreement with the experiment of Kell, McLaurin, and Whalley (performed at temperatures from 423 to 723 K) that the successive entropy of the trimer is -17 cal mol^{-1}K^{-1} and the trimer has the linear structure [51,52]. Similarly, we can expect that higher clusters may have open structures at very high temperatures (for $T > {\sim}500$ K), while at reasonably high temperatures the
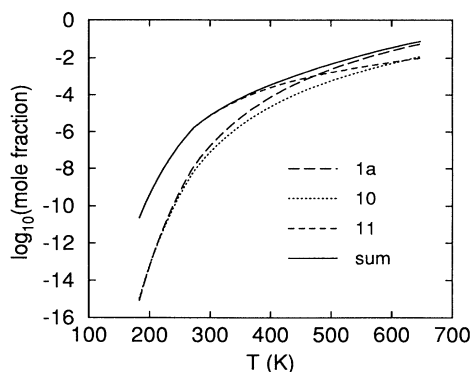
FIG. 6. Mole fractions of the three stable conformers of the trimer [i.e., linear (1a), unidirectional cyclic (11), and nonunidirectional cyclic (10) structures] in vapor with respect to the boiling or subliminating temperature (T) or the vapor pressure (P). See text.

open structures of small cyclic clusters (such as trimers) with a few branched monomers or dimers may be more populated than the same size of closed structures. However, at low temperatures (for $T < \sim 300$ K) the clusters with closed structures (with minimum-energy structures at 0 K) will be highly populated. In order to extend our discussion to the condensed phenomena, the most important free-energy correction would come from a numerous number of multiminima along with potential flatness for very large n, which we do not discuss in the present paper.

V. CONCLUDING REMARKS

We predicted the thermodynamic quantities of the water clusters. Along the vapor pressures of the condensed phase, the mole fractions of small cyclic water clusters (for $n = 1-6$), D_{2d} octamer, and the isoenergetic hexamer and octamer have been predicted. However, the results may be only reliable below ~ 300 K, because the entropy was calculated with the HF harmonic frequencies without considering not only the potential flatness but also multiminimum structures. Nevertheless, we reported the results up to the range of the critical temperature of water, so that we may have a rough idea of the distribution of a certain cluster which keeps almost the original minimum-energy structure. The mole fractions of higher clusters increase with increasing temperature or pressure. The logarithm of the mole fraction of each cluster changes almost linearly with the logarithm of the vapor pressure. In vapor the higher clusters can hardly be populated in the equilibrium state. On the other hand, in a nonequilibrium system with insufficient water molecules the condensation of the higher clusters can be prohibited, thus large mole fractions of the higher clusters may be obtained.

The entropy increment of the cyclic pentamer relative to the cyclic tetramer is found to be particularly small; thus, the cyclic pentamer shows thermodynamically unusual characteristics. At high temperatures, the cyclic pentamer can be more populated than the cyclic tetramer. We also find that at high temperatures higher clusters tend to have the linearlike or open structures due to the entropic energy gain.

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